

# Phase diagram of disordered spin-Peierls systems

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(February 1, 2008)*

We study the competition between the spin-Peierls and the antiferromagnetic ordering in disordered quasi-one-dimensional spin systems. We obtain the temperature vs disorder-strength phase diagram, which qualitatively agrees with recent experiments on doped CuGeO<sub>3</sub>.

PACS numbers: 64.70Kb, 75.10Jm

The discovery of the first inorganic spin-Peierls (SP) material CuGeO<sub>3</sub> opened the possibility to study the influence of doping on the SP transition [1]. The recently obtained phase diagram of doped CuGeO<sub>3</sub> has several surprising features [2–5]. It turns out that doping, while suppressing the SP state, at the same time induces long-range antiferromagnetic (AF) order, with the Neel temperature initially increasing with the doping concentration. Furthermore, a doping range is found where SP and AF order coexist.

At first glance, it seems very strange that disorder (doping) may lead to the enhancement of some order parameter (in this case the AF one). Also, the coexistence of the dimerized SP state, in which spins are bound into singlets, with a spontaneous sublattice magnetization that requires the presence of free spins, is rather puzzling. In this Letter we address both these issues and obtain a phase diagram that is very similar to the experimental one. We also predict a new phenomenon: a re-entrance transition from the dimerized SP state back into the undimerized state with decreasing temperature.

Theoretically, the possibility of long-range magnetic order in doped SP systems was discussed in Refs. [7–9], where the lattice was treated classically and it was assumed that impurities “cut” the spin chains into finite segments. It was argued that the lattice relaxation in these segments results in the appearance of regions with a suppressed dimerization (close to impurities in the model of Ref. [7], or centered at kinks in the lattice dimerization in Refs. [8,9]). The AF correlations that develop in these regions may, in principle, stabilize an inhomogeneous state in which the SP and AF orders coexist. The enhancement of the magnetic susceptibility by disorder-induced kinks was also discussed in Ref. [10]. Although these considerations provide a qualitative understanding of the magnetic ordering in doped SP materials, the description of the thermodynamics of the mixed SP+AF state within the same approach is complicated and so far has not been given.

In this Letter we consider a model that does allow for a detailed study of the competition between the SP and AF phases in the presence of disorder. Instead of considering disorder that randomly cuts chains into finite segments,

we assume that doping results in small fluctuations of the spin-exchange constants on many bonds. Furthermore, we treat the lattice and the interchain interactions in the “chain mean field” approximation [11]. Then, the effective single-chain Hamiltonian reads:

$$H_s = \sum_n J_{n,n+1} \mathbf{S}_n \cdot \mathbf{S}_{n+1} - h \sum_n (-)^n S_n^z, \quad (1)$$

where the exchange constants have the form:

$$J_{n,n+1} = J_0 + (-)^n \Delta + \delta J_{n,n+1}. \quad (2)$$

Here,  $\Delta$  is the average value of the SP dimerization, and  $\delta J_{n,n+1}$  is the random contribution due to doping. The antiferromagnetic order parameter  $h$  in Eq.(1) is the amplitude of the alternating magnetic field created by the neighboring chains. The two order parameters  $\Delta$  and  $h$  have to be found in a self-consistent way: the dimerization amplitude  $\Delta$  is proportional to the alternating part of  $\langle\langle \mathbf{S}_n \cdot \mathbf{S}_{n+1} \rangle\rangle$ , while  $h$  is proportional to the alternating part of  $\langle\langle S_n^z \rangle\rangle$ , where  $\langle\langle \dots \rangle\rangle$  denotes the thermal and disorder average.

Unfortunately, analytical expressions for these disorder averages within the model Eq.(1) are not known and their numerical calculation at present cannot be done efficiently enough to solve the self-consistency equations. This motivates us to simplify the model, by considering only the XY part of the spin-spin interaction, *i.e.*, we substitute  $\mathbf{S}_n \cdot \mathbf{S}_{n+1}$  by  $S_n^x S_{n+1}^x + S_n^y S_{n+1}^y$ . In the absence of disorder the XY model is known to provide a reasonable description of both the AF and the SP state [12,13]. Moreover, as follows from numerical and analytical studies, in the presence of disorder the low-temperature behavior of the chain susceptibility to uniform and alternating magnetic fields is universal, *i.e.*, independent of the anisotropy of the spin exchange [14–16].

By means of the Jordan-Wigner transformation the XY model can be mapped on a free-fermion Hamiltonian. Then,  $J_{n,n+1}/2$  becomes the fermion hopping amplitude between sites  $n$  and  $n+1$ , while  $h$  becomes the amplitude of an alternating on-site potential. The coexistence of SP and AF order in the XY model corresponds to the coexistence of a Peierls dimerization and an on-site charge density wave in the spinless fermion model.

In the weak-coupling and weak-disorder limit, *i.e.*, for  $\Delta, h, \delta J \ll J_0$ , we now introduce a continuum description of the chain (cf. Ref. [17]). The Hamiltonian then becomes:

$$H_f = \int dx \psi^\dagger(x) \left[ \sigma_3 \frac{v_F}{i} \frac{d}{dx} + \sigma_1 (\Delta + \eta(x)) + \sigma_2 h \right] \psi(x), \quad (3)$$

where  $\sigma_a$  ( $a = 1, 2, 3$ ) are the Pauli matrices. The first term in the Hamiltonian  $H_f$  describes the free motion of the fermions with the Fermi velocity  $v_F = aJ_0$ , while the second and the third terms describe the backward scattering caused by the dimerization, the disorder, and the staggered magnetic field. The disorder  $\eta(x)$  is related to the disorder in the spin-exchange constants by

$$\eta(2na) = \frac{1}{2} (\delta J_{2n-1, 2n} - \delta J_{2n, 2n+1}), \quad (4)$$

where  $a$  denotes the lattice constant in the chain direction. We will assume white noise disorder with a correlator:

$$\langle \eta(x) \eta(y) \rangle = A \delta(x - y), \quad (5)$$

which corresponds to the statistical independence of the variations of the exchange couplings on different bonds in the discrete model Eq.(1).

In the absence of a magnetic field ( $h = 0$ ), the disorder-averaged density of single-fermion states  $\rho(\varepsilon)$  of the Hamiltonian Eq.(3) was found analytically in Ref. [18]. The density  $\rho(\varepsilon)$  is a symmetric function of the energy  $\varepsilon$ . Its form depends crucially on the parameter  $g = A/(v_F \Delta)$ . For  $g < 2$  the density of states has a pseudogap (a Peierls gap filled by disorder-induced states), while for  $g > 2$  (strong disorder) the pseudogap disappears and  $\rho(\varepsilon)$  diverges at  $\varepsilon = 0$  ( $\rho(\varepsilon) \propto |\varepsilon|^{\frac{2}{g}-1}$  at  $|\varepsilon| \ll \Delta$ ).

A nonzero alternating magnetic field mixes the  $h = 0$  eigenstates with opposite energies and transforms the pair of eigenstates with energies  $\pm \varepsilon$  into a pair of eigenstates with energies  $\pm \sqrt{\varepsilon^2 + h^2}$ . Therefore, the disorder-averaged  $\Omega$ -potential ( $\Omega_f = -T \langle \ln \Xi_f \rangle$ ,  $\Xi_f$  being the partition function of the grand-canonical ensemble of fermions with zero chemical potential) is given by

$$\Omega_f = -\frac{2}{\beta} \int_0^W d\varepsilon \rho(\varepsilon) \ln \left[ 2 \cosh \left( \frac{\beta \sqrt{\varepsilon^2 + h^2}}{2} \right) \right], \quad (6)$$

where  $W$  is the energy cut-off. The two order parameters,  $\Delta$  and  $h$ , satisfy the self-consistency equations:

$$\Delta = -\lambda_\Delta \langle \langle \sigma_1 \rangle \rangle = -\lambda_\Delta \frac{\partial \Omega_f}{\partial \Delta}, \quad (7)$$

$$h = -\lambda_h \langle \langle \sigma_2 \rangle \rangle = -\lambda_h \frac{\partial \Omega_f}{\partial h}, \quad (8)$$

where  $\lambda_\Delta$  and  $\lambda_h$  are the corresponding coupling constants describing the interchain interactions.

In the absence of disorder,  $\Omega_f$  depends on  $\Delta$  and  $h$  only through the combination  $\sqrt{\Delta^2 + h^2}$ . As a result, the two self-consistency equations acquire the same (BCS) form; as, however, they have different coupling constants, they cannot be satisfied simultaneously, unless  $\lambda_\Delta = \lambda_h$ . Thus, in agreement with previous studies [19], we find that in the absence of disorder the AF and SP phases cannot coexist and the phase with the larger coupling constant is realized. A competition between these two phases always exists in spin chain materials and some special conditions, such as a strong spin-phonon coupling [13] or a significant next-nearest-neighbor interaction [20], are necessary for the SP state to win. This explains why the number of SP materials is small.

Disorder in the spin-exchange constants suppresses the dimerized state by filling the SP gap with single-fermion states and thus reducing the energy gain due to dimerization. At the same time, these disorder-induced states enhance the antiferromagnetic susceptibility of the chains: The effect of an alternating magnetic field is strongest for the fermionic states with  $|\varepsilon| \leq h$ , as the occupied state with energy  $-|\varepsilon|$  is pushed down to  $-\sqrt{\varepsilon^2 + h^2}$ . The higher is the density of states near  $\varepsilon = 0$ , the more energy is gained when AF order appears. Within the mean field approximation, this enhancement of the chain magnetic susceptibility due to disorder results in an increase of the Neel temperature.

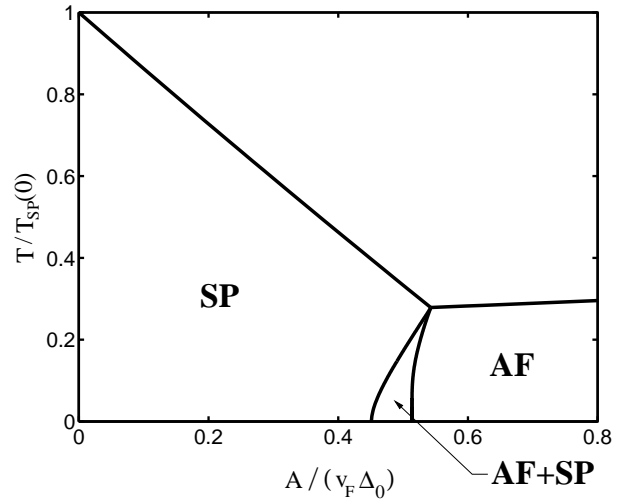


FIG. 1. The phase diagram of the disordered SP system described by Eqs.(3),(7), and (8) for  $\lambda_\Delta > \lambda_h$ . The dimensionless disorder strength  $A/(v_F \Delta_0)$  is proportional to the concentration of dopands  $x$  (see discussion in the text). The temperature is measured in the units of the SP transition temperature at zero disorder.

From the above we conclude that for  $\lambda_h > \lambda_\Delta$  the SP state is less favorable than the AF state at all values of the disorder strength  $A$ . If, on the other hand,

$\lambda_\Delta > \lambda_h$ , a much richer phase diagram arises, as is observed in Fig. 1. This diagram was obtained by numerically solving Eqs. (7) and (8) for  $\lambda_\Delta$  and  $\lambda_h$  such that  $T_N^0(0)/T_{SP}^0(0) = 1/4$ , where  $T_{SP}^0(A)$  is the SP transition temperature at  $h = 0$  and  $T_N^0(A)$  is the Neel temperature at  $\Delta = 0$ . Four phases appear: SP, AF, mixed SP+AF and disordered, separated by second order transition lines. At low temperature and weak disorder the system is in the SP state. The SP temperature  $T_{SP}(A)$  decreases almost linearly with the disorder strength. In particular, it can be shown that at small  $A$

$$T_{SP}(A) = T_{SP}(0) \left( 1 - C \frac{A}{v_F \Delta_0} \right), \quad C = \frac{\pi^2}{4\gamma} \approx 1.39, \quad (9)$$

where  $\Delta_0$  is the value of  $\Delta$  for  $T, A = 0$ , and  $\gamma = 1.78 \dots$ , is the exponential of Euler's constant.

Above some critical disorder strength  $A_N$ , the system undergoes at  $T_N(A) < T_{SP}(A)$  a second (Neel) transition into the mixed state, in which the SP and AF orders coexist. This coexistence region becomes narrower when  $\lambda_h$  approaches  $\lambda_\Delta$ .  $T_N$  rapidly increases with the disorder strength until at some  $A = A_*$  it becomes equal to the SP transition temperature:  $T_{SP}(A_*) = T_N(A_*) = T_*$ . Above  $A_*$  only AF long-range order exists and the Neel temperature continues to grow slowly with the disorder strength.

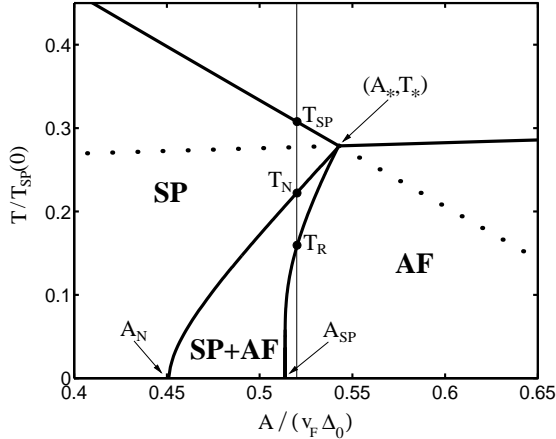


FIG. 2. Detail of the phase diagram Fig. 1. The vertical line  $A/(v_F \Delta_0) = 0.52$  passes through three phase-transition points: the SP transition temperature  $T_{SP}$ , the Neel temperature  $T_N$ , and the temperature of re-entrance into the undimerized state  $T_R$ . Dotted lines show  $T_{SP}^0$  for  $A > A_*$  (the SP transition temperature calculated at  $h = 0$ ) and  $T_N^0$  for  $A < A_*$  (the Neel temperature calculated at  $\Delta = 0$ ).

The surprising feature of our phase diagram is the fact that the disorder strength  $A_{SP}$  at which the dimerization disappears at zero temperature, is smaller than  $A_*$ . This implies that for  $A_{SP} < A < A_*$  the system experiences three consecutive transitions as the temperature goes down (see Fig.2): first the SP transition, next the Neel transition, and then the “anti-spin-Peierls” transition, at

which the SP order disappears. The re-entrance into the undimerized state occurs, because the rapid growth of the AF order parameter below the Neel temperature suppresses the SP state.

The existence of a re-entrance transition can be further elucidated by considering the Ginzburg-Landau expansion of  $\Omega = \Omega_f + \frac{\Delta^2}{2\lambda_\Delta} + \frac{h^2}{2\lambda_h}$  near the multicritical point  $(T_*, A_*)$ :

$$\Omega = \alpha_\Delta (T - T_{SP}^0(A)) \Delta^2 + \frac{b_\Delta}{2} \Delta^4 + \alpha_h (T - T_N^0(A)) h^2 + \frac{b_h}{2} h^4 + c \Delta^2 h^2. \quad (10)$$

In Eq.(10) the coefficients  $\alpha_\Delta, \alpha_h > 0$ . Furthermore, the stability of the system described by Eq.(10), requires  $b_\Delta, b_h$ , and  $D \equiv b_\Delta b_h - c^2$  to be positive.

In the presence of a dimerization (at  $A < A_*$ ) the Neel temperature becomes:

$$T_N(A) = T_N^0(A) - \frac{c}{\alpha_h} \Delta^2. \quad (11)$$

As the dimerization suppresses the AF state,  $c > 0$ . Similarly, one can find a temperature  $T_R(A)$ , at which  $\Delta$  becomes zero at nonzero  $h$ :

$$T_R(A) = T_{SP}^0(A) - \frac{c}{\alpha_\Delta} h^2, \quad (12)$$

which is the temperature of the re-entrance into the undimerized state.

To obtain the dependence of  $T_N(A)$  and  $T_R(A)$  on the disorder strength, we find  $\Delta$  and  $h$  that minimize  $\Omega$  and substitute them into Eqs.(11) and (12). The result is:

$$T_N(A) \approx T_* + (A - A_*) \left[ \frac{c\alpha_\Delta \frac{dT_{SP}^0}{dA} - b_\Delta \alpha_h \frac{dT_N^0}{dA}}{c\alpha_\Delta - b_\Delta \alpha_h} \right]_{A=A_*}, \quad (13)$$

$$T_R(A) \approx T_* + (A - A_*) \left[ \frac{c\alpha_h \frac{dT_N^0}{dA} - b_h \alpha_\Delta \frac{dT_{SP}^0}{dA}}{c\alpha_h - b_h \alpha_\Delta} \right]_{A=A_*}.$$

From Eq.(13) and the fact that  $T_N^0(A)$  increases with  $A$ , while  $T_{SP}^0(A)$  decreases, it is easy to find that for

$$c > b_h \frac{\alpha_\Delta}{\alpha_h} \quad (14)$$

both  $T_N(A)$  and  $T_R(A)$  increase linearly with disorder at  $A < A_*$  and  $T_R(A) < T_N(A)$ . Therefore, inequality (14) is the condition for the existence of the re-entrance transition. In our model, its validity can be checked analytically for  $\lambda_h \rightarrow \lambda_\Delta$ , in which case  $A_* \rightarrow 0$ ,  $\alpha_h \rightarrow \alpha_\Delta$ , and  $c \rightarrow 2b_h$ . Our numerical calculations suggest that condition (14) is satisfied for all  $\lambda_h < \lambda_\Delta$ .

Next we compare our phase diagram to experimental data. At small dopand concentrations  $x$ , the observed SP transition temperature in  $\text{Cu}_{1-x}\text{Zn}_x\text{GeO}_3$  is described by

$$T_{SP}(x) = T_{SP}(0)(1 - \alpha x), \quad (15)$$

where  $\alpha \sim 14$  [2]. To compare this to our result Eq.(9), we have to relate the disorder strength  $A$  to the dopand concentration  $x$ . This can be done by assuming that the substitution of Cu by Zn changes the spin exchange constant by an amount  $\sim J_0$ . From Eqs. (4) and (5) we then obtain:

$$A \sim aJ_0^2 x. \quad (16)$$

Equation (9) then reduces to Eq.(15) with

$$\alpha \sim \frac{J_0}{\Delta_0} C \sim 9. \quad (17)$$

Keeping in mind that in our model doping-induced large fluctuations in some (randomly chosen) spin-exchange constants are replaced by small fluctuations on all bonds, the agreement with experiment is good. Also the even stronger suppression ( $\alpha \sim 50$ ) of the SP phase in Si doped CuGeO<sub>3</sub> [3–6] may be understood: Si, substituting Ge, is located between two CuO<sub>2</sub>-chains and thus influences two chains simultaneously [8].

One not quite satisfactory aspect of our model is that for realistic values of parameters the critical doping concentration  $x_c$  at which AF order appears, seems to be too large as compared with experiment [6]. This may be understood from the following considerations: Disorder enhances the AF susceptibility of spin chains by filling the SP gap with low-energy spin excitations. As was shown in Ref. [21], with highest probability the excited states with energy  $\varepsilon \ll \Delta$  occur for disorder fluctuations  $\eta(x)$  that have the form of a kink-antikink pair. For such a fluctuation, the order parameter  $\Delta(x) = \Delta + \eta(x)$  has reversed sign in a domain of length  $R = (v_F/\Delta) \ln(2\Delta/\varepsilon)$  between the kink and the antikink. The kink and antikink, being fractionally charged objects [22], each carry spin  $\frac{1}{2}$ , which together form a weakly bound singlet. A low-energy excited state is then obtained by exciting this singlet into a triplet. These weakly bound spins do not contribute to the dimerization, but they can give rise to AF ordering. However, for weak disorder (small  $x$ ), the density of kink-antikink fluctuations is exponentially small in our model, implying that a critical dopand concentration  $x_c$  is necessary for AF order to appear. It can be argued that  $x_c$  would be lowered if the model would allow for large fluctuations on some randomly chosen bonds, in which case the kink density  $\propto x$  [8,9]. Such an extension of the model, however, makes it much harder to obtain the complete phase diagram, as it becomes impossible to make the continuum approximation.

To summarize, we obtained the phase diagram of a disordered SP system, described by a mean-field model. We showed that disorder results in a strong suppression of the SP state and gives rise to AF long range order, which in a certain range of the disorder strength coexists with

the dimerization. These results are in agreement with the experimental data on doped CuGeO<sub>3</sub>. Finally, our results indicate the possibility of a re-entrance transition from the dimerized SP state back into undimerized state.

This work is supported by the "Stichting voor Fundamenteel Onderzoek der Materie (FOM)". We would like to thank Prof. J.-P. Renard for providing us with the manuscript of Ref. [6] prior to its publication.

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- [1] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).
- [2] M. Hase *et al.*, Phys. Rev. Lett. **71**, 4059 (1993).
- [3] J.-P. Renard *et al.*, Europhys. Lett. **30**, 475 (1995).
- [4] L. P. Regnault, J. P. Renard, G. Dhallenne, and A. Revcolevschi, Europhys. Lett. **32**, 579 (1995).
- [5] M. Hiroi *et al.*, Phys. Rev. B **55**, R6125 (1997).
- [6] B. Grenier *et al.*, to be published in Phys. Rev. B.
- [7] H. Fukuyama, T. Tanimoto, and M. Saito, J. Phys. Soc. Japan, **65**, 1182 (1996).
- [8] D. Khomskii, W. Geertsma, and M. Mostovoy, Czech. Journ. of Phys., **46**, Suppl. S6, 3229 (1996).
- [9] M. Mostovoy and D. Khomskii, Z. Physik B **103**, 209 (1997).
- [10] M. Fabrizio and R. Mélin, Phys. Rev. Lett. **78**, 3382 (1997).
- [11] Y. Imry, P. Pincus, and D. Scalapino, Phys. Rev. B **12** 1978 (1975).
- [12] L. N. Bulaevskii, Zh. Eksp. Theor. Fiz. **43**, 968 (1962) [Sov. Phys. JETP **16**, 685 (1963)].
- [13] L. N. Bulaevskii, A. I. Buzdin, and D. I. Khomskii, Solid State Commun. **27**, 5 (1978).
- [14] C. Dasgupta and S. K. Ma, Phys. Rev. **22**, 1305 (1980).
- [15] D. Fisher, Phys. Rev. B **50**, 3799 (1994).
- [16] R. A. Hyman, K. Yang, R. N. Bhatt, and S. M. Girvin, Phys. Rev. Lett. **76**, 839 (1996).
- [17] H. Takayama, Y. R. Lin-Liu, and K. Maki, Phys. Rev. **21**, 2388 (1980).
- [18] A. A. Ovchinnikov and N. S. Erikhman, Zh. Eksp. Theor. Fiz. **73**, 650 (1977) [Sov. Phys. JETP **46**, 340 (1977)].
- [19] S. Inagaki and H. Fukuyama, J. Phys. Soc. Japan **52**, 3620 (1983).
- [20] G. Castilla, S. Chakravarty, and V. J. Emery, Phys. Rev. Lett. **75**, 1823 (1995).
- [21] M. V. Mostovoy and J. Knoester, Phys. Lett. A. **235**, 535 (1997).
- [22] See, *e.g.*, R. Jackiw and J. R. Schrieffer, Nucl. Phys. B **190**, 253 (1981).